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SEMICONDUCTORS A^{III}B^{VI}

by

G.A. Akhundov, G.B. Abdullaev, et al.



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А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ы; e elsewhere.
When written as ё in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian English

rot curl
lg log

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SEMICONDUCTORS $A^{\text{III}}B^{\text{VI}}$

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M. Kh. Aliyeva, Ye. S. Guseynova and I. A. Gasanova*

Semiconductors $A^{\text{III}}B^{\text{VI}}$ crystallize in laminated or chain structures and contain nine valence electrons in each molecule [1]. Connection in the layers and the chains is predominantly covalent, and Van der Waal between the layers and the chains. Calculated data of the energy spectrum of these compounds are absent, and the available experimental studies are insufficient for understanding of the zone structures. We have obtained and studied single crystals of GaS, GaSe, GaTe, InSe, TiSe. These semiconductors possess a number of specific properties. Some of them proved to be highly photosensitive, an increase of the electrons and holes in TiSe was discovered by phonons, the electron mobility in InSe rises as T^{+6} [2], and at low temperatures the edge of fundamental absorption of gallium chalcogenide has a linear structure (3-4), very thin single-crystal layers or chains are easily split off from large single crystals.

Single crystals of n -TiSe and compensated GaSe, InSe are obtained with the introduction of admixtures Sn, Ge, or Si. Point-contact diodes were prepared on a base of n -TiSe and their properties were studied at different temperatures (5).

Single crystals of GaS, GaSe, InSe are interesting objects for studying of the phenomenon of injection, luminescence, electroluminescence, etc.

The results of the studies of the electric, photoelectric and optical properties of single crystals GaS, GaSe, GaTe, InSe and TiSe are presented in the given report.

Single crystals of p - and n -TiSe with a diameter of 15 mm and with a length of 80 mm were obtained by the method of horizontal or vertical zone melting [6-7]. Single crystals of GaS, GaSe, GaTe and InSe with a diameter of 12 mm and a length of 50 mm were grown by slow cooling with constant temperature gradient (8).

The electrical properties

Although the electrical properties of a number of $A^{III}B^{VI}$ compounds were studied by us, here we stop at TlSe.

Fig. 1 presents the temperature dependence of electroconductivity $\sigma(a)$ and the Hall constant $R(b)$ of five annealed single crystals p -TlSe with different concentrations of admixtures in an interval of $80^\circ + 570^\circ K$ along the axis $[001]$. Crystals, characterized by curves 1-5, had admixture concentrations of 10^{18} - $6.5 \cdot 10^{13} \text{ cm}^{-3}$.

Page 108

The temperature dependence of the Hall mobility of holes μ_p is calculated in the same crystals p -TlSe. At sufficiently high temperatures, approximately $\mu_p \sim T^{-3/2}$, which indicates a scattering of charge carriers on acoustic oscillations. Moreover, with a lowering of the admixture concentrations the region of phonon scattering expands and with a concentration of $6 \cdot 10^{13} \text{ cm}^{-3}$ encompasses almost the entire region of measurement.

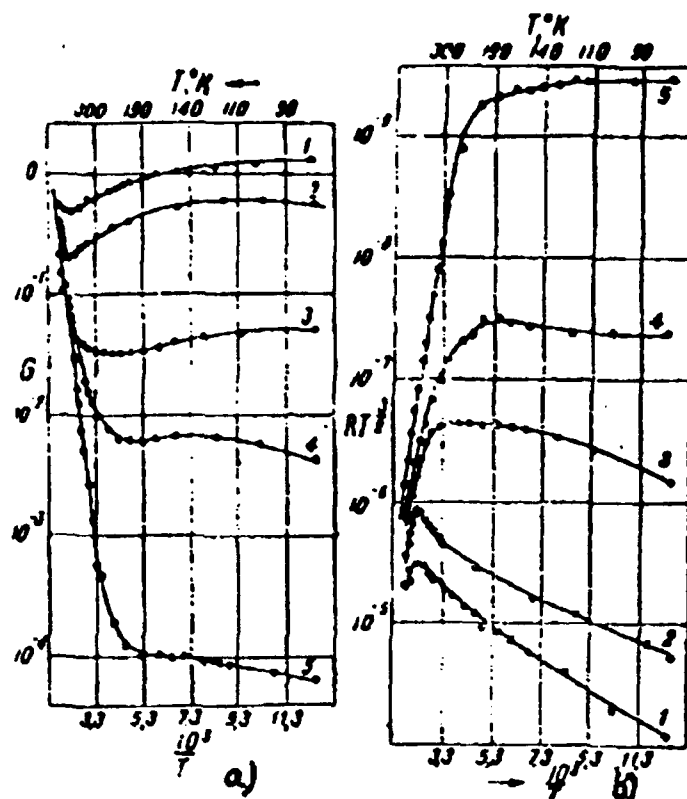


Figure 1. Temperature dependence of electroconductivity (a) and the Hall constant (b) of TiSe.

Carrier concentrations temperatures and thermal emf (a) of single crystals of TiSe were studied over a wide range. A temperature dependance (α) was constructed for nine samples of *p*- and *n*-TiSe in an interval of 80-570°K (Fig. 2). Crystals 1-6 of them, with admixture concentrations of $6.5 \cdot 10^{17}$, $6 \cdot 10^{16}$, $9 \cdot 10^{15}$, $5 \cdot 10^4$, $2 \cdot 10^{14}$ and $6.5 \cdot 10^{13}$ cm⁻³ had *p*-conductivity. α for the indicated samples remains positive also in the intrinsic conduction region and decreases only in absolute value with an increase in temperature. The remaining three samples (curves 7-9), having concentrations at 300°K of $6.8 \cdot 10^{14}$, $2.6 \cdot 10^{15}$ and $8 \cdot 10^{15}$ cm⁻³, possessed *n*-conductivity. The intrinsic conduction region in the measured temperature range was reached only for one of the samples of *n*-TiSe, in which was observed a sign inversion (curve 7).

Page 109

There is special interest in the low-temperature region, beginning from 160°K, where in some *n*- and *p*-TiSe samples, possessing a comparatively small concentration of current

carriers, α strongly rises in absolute value, with a decrease in temperature, to values of (2-7 mv/deg), which considerably exceed the predictions of usual electronic theory. This we explain by the presence of the effect of the entrainment of current carriers by phonons. During the determination of the temperature dependence of the phonon part of the thermal emf α_ϕ the additive relationship $\alpha = \alpha_\Sigma + \alpha_\phi$ was used, since the concentration of current carriers in these samples is sufficiently small in order to disregard their scattering effect on the phonons. The values of diffusion component α_Σ were determined, in this case, by the extrapolation of the curved temperature dependence of the common thermal emf above 160°K on the basis of the experimental data of the Hall coefficient according to the formula:

$$\alpha_\Sigma = \frac{K}{e} [\ln RT^{3/2} - 9.6]$$

Thus, it was established that with the advent of the effect of entrainment effect the temperature dependence α_ϕ intensifies from $T^{-1.4}$ to $T^{-3.3}$ with a decrease in temperature, which corresponds to a change in the temperature dependence of the relaxation time of acoustic phonons τ_ϕ from $T^{-1.9}$ to $T^{-3.8}$ upon consideration that $\tau \sim T^{3/2}$. It is easy to ascertain that the indicated dependence is in a good agreement with the theory of the entrainment effect of current carriers by phonons for the semiconductors with tetragonal symmetry [9]. Actually, according to this theory, if the accidental intersection of oscillatory branches does not occur on the plane $K_x=0$ ($K_y=0$), then for the tetragonal crystal the dependence of the relaxation time of longitudinal acoustic phonons τ_ϕ on temperature (T) and quasi-momentum (q) takes

the form: $\tau_\phi = \frac{h^2 v_3^2 P}{K^2} q^{-2} T^{-3}$. Taking into account that the quasi-momentum of the

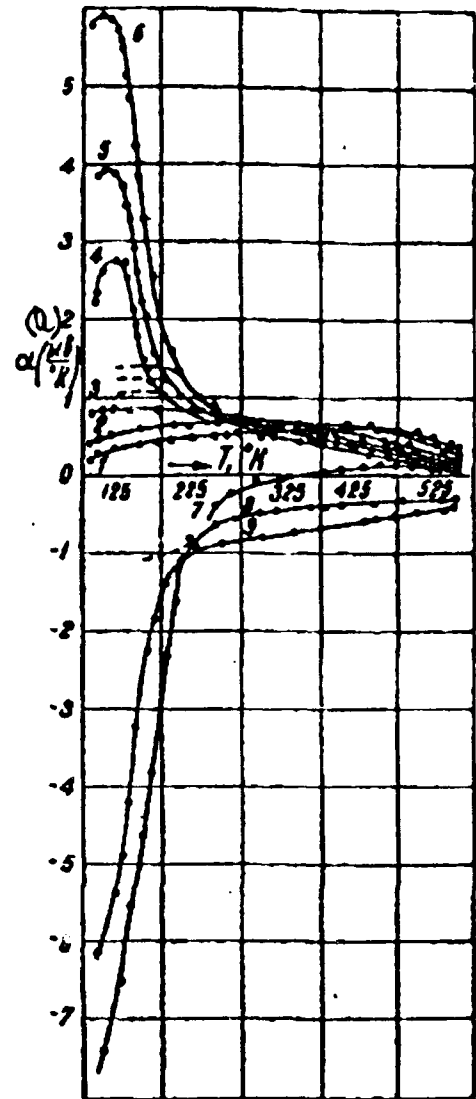


Figure 2. The dependence of the coefficient of thermal emf of TlSe on temperature
Key: (a). α (Mv/°K).

primary part of the long-wave phonons $q = \frac{(2m^*_{\kappa} T)^{1/2}}{h^*}$ for the crystals with a tetragonal

structure we receive,

$$\tau_{\phi} = \frac{h^4 v_3^2 \rho}{2m^*_{\kappa}{}^3} T^{-4} \sim T^{-4},$$

as is evident, it is sufficiently close to the dependence observed during the experiment.

Page 110

The fundamental parameters of TlSe were determined from the experimental data: the width of the forbidden band $\Delta E = 0.57 \cdot 3.9 \cdot 10^{-3}$ of eV/grad, mobility relationship $b = \frac{\mu_n}{\mu_p} = 0.33$, the effective mass of the density of the electron

states $m_n^* = 0.3m_0$ and holes $m_p^* = 0.6m_0$

Photoelectric properties

Fig. 3 shows the spectral distribution of photoconductivity for five compounds at 300°K. The width value of the forbidden band of the indicated compounds, calculated on $\lambda_{1/2}$, is given in Table 1. The spectral and lux-ampere characteristics of the single crystals obtained were studied at different temperatures.

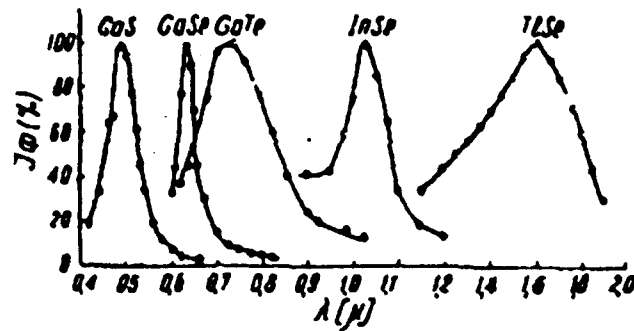


Figure 3. The spectral distribution of the photoconductivity at 300°K

Table 1

Crystals	ρ Ω cm	σ E_{OT} (ev)	σ E_* (e ϕ)
GaS	10^{10} - 10^{11}	2.53	2.38
GaSe	10^2 - 10^4	1.97	1.93
GaTe	$4 \cdot 10^2$	1.67	1.5
InSe	$2 \cdot 10^2$	1.2	1.2
TlSe	1-40	0.7	0.67

Is experimentally studied the kinetics of its own photoconductivity of single crystals GaSe and TlSe. It is discovered, that relaxation curves consisting of two components: "slow" and "rapid".

Fig. 4 shows lux-ampere dependence of the amplitude of the complete photocurrent (curves 1), slow (curves 2) and rapid components (curves 3) for GaSe (a) and TlSe (b). By increasing the light intensity the amplitude of the slow component rises nonlinearly, achieving saturation, whereas the rapid component increases approximately linearly. With an increase in the intensity of constant illumination the slow component decreases and finally disappears.

The temperature dependencies of the time constant of the slow component of decay in the photoconductivity for GaSe (a) and TlSe (b) are represented in Fig. 5a and b, respectively.

As is evident, the time constant of decay in the slow component at low temperatures is changed insignificantly for both crystals, and with high it decreases exponentially with an increase in the temperature. Under the conditions of the experiment the value of the constant decay time did not depend on the intensity of light and illumination.

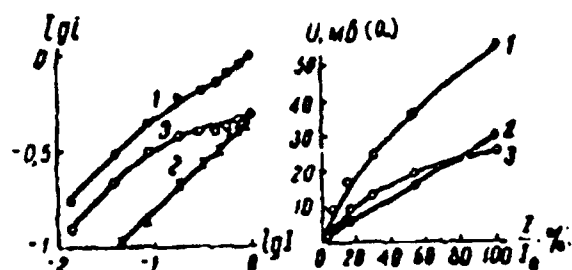


Figure 4. Lux-ampere characteristic of stationary photoconductivity and its components
Key: (a). mV.

The laws given above are well explained on the basis of a model with one "saturated" level of single adhesion (taking into account recombination through them). Corresponding calculations of this model show that the time constant of decay is expressed by the formula:

$$\tau_c = \frac{1}{\gamma_n N_{cm} + \gamma_p p_0},$$

where τ_n, τ_p - respectively the coefficients of electron trapping and holes at the trapping level; p_0 - equilibrium concentration of holes in the valence band;

$N_{cm} = N_c e^{-\Delta E_m / kT}$ (N_c - effective position density in the conduction band); ΔE_m - depth of

the trapping level occurrence.

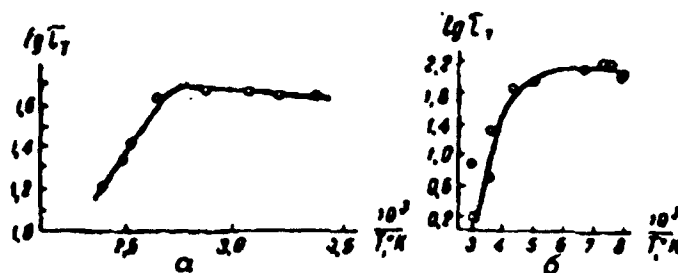


Figure 5. Temperature dependence of the photoconductivity decay time constant.

From the formula it follows that at low temperatures ($\gamma_m N_{cm} \ll \gamma_p p_0$) the intensity of the thermal excesses is small and the decay time constant is determined only by the process of the recombination of electrons with the equilibrium holes of valence band seized at the trapping level - and therefore is changed insignificantly (in this temperature segment p_0 it depended weakly on temperature). On the contrary, in the area of "high" temperatures (when $\gamma_m N_{cm} \gg \gamma_p p_0$) the intensity of the thermal excesses of electrons from the levels in the conduction band considerably exceeds the direct recombination of these electrons with the free holes and time constant decreases exponentially with an increase in temperature.

The comparison of the formulas obtained with the experimental dependencies determined the parameters of trapping levels for both compounds (Table 2).

Page 112

Table 2

Crystals	Degree of the level position, eV	Effective capture cross-section for electrons, cm^2	Effective capture cross-section for holes cm^2	Level concentrations, cm^{-3}
GaSe	0.32	$4 \cdot 10^{-23}$	$1.5 \cdot 10^{-25}$	$2 \cdot 10^{13}$
TlSe	0.15	$4 \cdot 10^{-15}$	$3 \cdot 10^{-21}$	$1.5 \cdot 10^{14}$

The spectrum of the admixed photoconductivity of the single crystals of gallium selenide was studied and a considerable photosensitivity in the region to three microns was discovered (Fig. 6), determined by the presence of three types of "emitter" levels, situated at 0.4; 0.56; and 0.71 eV from the ceiling of the valence band [10].

The presence of the three impurity levels is confirmed by the results on the study of the kinetics of admixed photoconductivity; during the excitation by light with a wavelength of 1.5; 1.9; and 2.2 μ relaxation curves are obtained, which consist, of three, two and one exponential curves, correspondingly, which unambiguously correspond to presence of three different emitter levels.

Two series of samples were taken from the single crystals InSe obtained for the measurements: a low-resistance with the specific resistance, measured along the layers, of about 200 $\Omega \cdot \text{cm}$ and a high-resistance with a specific resistance of about 10000 $\Omega \cdot \text{cm}$. The sign of current carriers in the crystals being studied, was determined according to the thermal emf, proved to be negative. All samples had high photosensitivity. Table 3 gives the values of specific sensitivity and multiplicity of change in the resistance with an illumination of 200 lux.

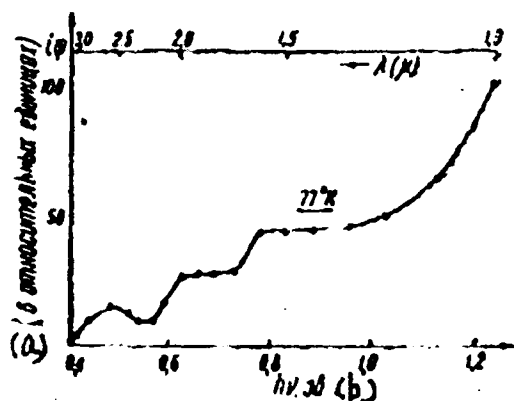


Figure 6. Spectral dependence of the photoconductivity of GaSe in region of admixed absorption.

Key: (a). relative units. (b). eV.

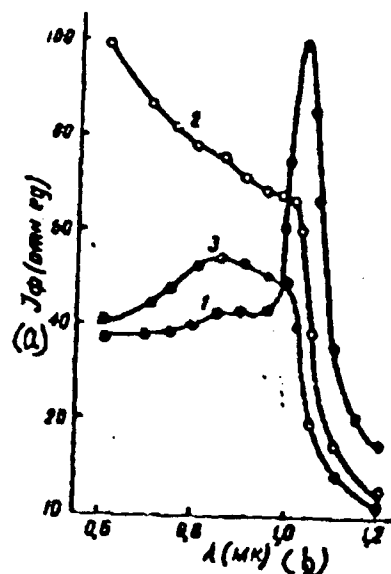


Fig 7. Spectral distribution of InSe photoconductivity: 1 - low resistance sample; 2 - high resistance sample; 3 - high resistance sample after prolonged exposure to darkness.

Key: (a). rel. un. (b). Ω .

Spectral distribution of photoconductivity InSe is represented in Fig. 7. Curve 1 relates to the low-resistance sample, curve 2 - to the high-resistance, curve 3 - to the same high-resistance sample after prolonged exposure to darkness. Low-resistance sample I has a sharply pronounced maximum of approximately 1.025μ .

Page 113

Table 3

Sample	Ωcm	$K \frac{\text{mA}}{\text{lm} \cdot \text{V}}$	$\frac{R_T}{R_C}$
low-resistance	200	63000	3.5
high-resistance	10^4	53000	15

For high-impedance samples, as can be seen from Fig. 6, their preliminary illumination influences the spectral distribution of photoconductivity. For prolonged exposure to darkness, the samples have a blurred maximum of approximately 0.85μ . Illumination of the sample leads not only to a total increase in photocurrent, but also changes its spectral distribution. A primary increase in the photocurrent in the short-wave region with $\lambda = 0.8 \mu$ is observed.

The change in the photoconductivity spectrum is reversed. With the illumination of the crystals, with prolonged exposure to darkness, their spectral characteristic corresponds to curve 2. An increase of the photoconductivity in the high-resistance samples with the illumination is connected, probably, with the high concentration of trapping centers for electrons. With illumination the trapping centers are filled with electrons, which leads to an increase in the photoconductivity during subsequent excitation. The primary increase in the photocurrent in the absorption band level ($\lambda < 0.8 \mu$) can be explained by the fact that the filling of trapping centers with white illumination occurs in essence near the sample surface. In these experiments the effect of measuring the light was excluded, since between the separate measurements the samples were located in the darkness for long time.

The value of the width of the forbidden band, calculated according to $\lambda_{1/2}$, is 1.2 eV for the high-resistance and 1.17 eV for the low-resistance samples.

Lux-ampere characteristics for the low-resistance samples obey the law $I_{\Phi} = A\Phi^n$, where $n=0.4-0.5$ with the illuminations 10-1000 lux. But for the high-impedance samples with the illumination of 200 lux the lux-ampere dependence is described by expression $I_{\Phi} = A\Phi^{0.5-0.6}$, and for $\Phi > 200$ lux $I_{\Phi} = A\Phi^{0.9}$.

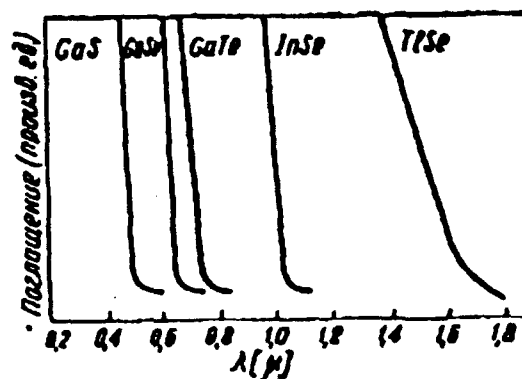


Figure 8
Spectrum of fundamental absorption at 300°K.
Key: * Absorption (prod. unit).

The spectral course of the absorption coefficient was determined by the spectra of light transmission by layers of different thickness. On the fundamental absorption edge for single crystals of InSe we obtain 1.2 eV for the width of the forbidden band, which will be coordinated with the value, obtained on the photoconductivity.

Fig. 8 depicts the fundamental absorption curves for five crystals $A^{III}B^{VI}$ at 300°K. The width of the forbidden bands, found from the curves in Fig. 7, is shown in Table 1.

The temperature coefficients of the width of the forbidden band for GaS and GaSe, on the temperature dependence of the absorption edge in an interval of 300-580°K, were $-7.2 \cdot 10^{-4}$ and $8 \cdot 10^{-4}$ eV/deg., respectively.

Page 114

During irradiation by electrons with an energy of 60 keV at room temperature a glow is observed in single crystals GaS, GaSe, ZnSe and GaTe, in the yellow, orange-red, red and dark-red regions of the spectrum respectively.

The authors consider it their pleasant duty to thank prof. D. N. Nasledova and Prof. S. M. Ryvkina for discussion of results and valuable council.

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